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Investigation of mass transfer in organic solvent nanofiltration membranes

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The development of solvent resistant membranes and membrane modules has established organic solvent nanofiltration (OSN) as a technically proven separation method. The advantages of OSN, such as mild processing conditions and low energy consumption, have led to intensive research and development of new membranes, which are stable in a wide range of organic solvents. Hence, these membranes offer numerous new application fields in pharmaceutical and chemical industry, either as a stand-alone operation or in combination with other unit operations as a part of a hybrid separation. Unfortunately, up to now, the implementations of membranes and membrane-assisted hybrid separations are still scarce. One of the main reasons for this is that design methods for OSN-processes are not yet well established. It calls for development of a reliable process model, based on fundamentals of thermodynamics and mass transfer in membrane polymers.

The state-of-art models for OSN are usually of semi-empirical nature, and parameters which are fitted to experimental data unify several different phenomena simultaneously such as, for example, diffusivity and solubility. Therefore such parameters have only limited physical significance. These results cannot be extrapolated or applied for a new separation problem. Therefore, this approach can hardly contribute to gaining more understanding concerning mass transfer in membranes. There are some attempts in literature which take different phenomena separately into account by introducing, for example, solubility parameters into flux equation [1]. However, the interactions between polymer membrane material, solvents and solutes that influence the separation efficiency are usually more complex and their description requires more sophisticated thermodynamic models.

In this work, a systematic approach is applied to identify these interactions and to predict the permeation and separation properties of asymmetric integral OSN membranes on the basis of thermodynamic properties of the membrane materials and solvents. Calculations of properties like the chemical potential in the solvent and membrane phase were performed using the PC-SAFT Equation of State (EoS) [2]. Two polyimides (Lenzing P84 and Matrimid 5218) which are commonly used as membrane materials in commercially available OSN membranes, and five organic solvents (hexane, ethyl acetate, 2-propanol, ethanol, and toluene) were chosen for our studies. Additionally, permeation of solvent mixtures was investigated. Furthermore in order to investigate rejection, paracetamol was chosen as solute.

Based on sorption measurements of all solvents in thick polyimide films, model parameters for PC-SAFT, as well as Stefan-Maxwell diffusion coefficients were determined [3]. The solvent flux was calculated based on the solution-diffusion theory using the Stefan-Maxwell equations and PC-SAFT EoS. Simulation results were validated by experimental investigations of a commercially available membrane STARMEM240^{TM} and further membranes, performed in a lab-scale Nanofiltration plant LStA60LM (Sima-Tec). The experiments were conducted in a pressure range from 5 - 35 bar, with a feed volume flow of 55 l/h, and at constant temperature of 25 °C. The concentration of paracetamol in the feed was varied up to 4 weight percent.

The obtained results show good agreement between predicted and measured performance of the Matrimid membrane Starmem240^{TM} for pure solvent flux. Furthermore the flux and rejection for ethanol/paracetamol mixture as well as for solvent mixtures could be described successfully. However, for P84 based membranes the predicted flux for pure solvents tends to be somewhat underestimated, which can be due to the fact that convective flux may contribute to the total flux in the investigated P84 membranes. Furthermore, especially for commercial membranes the exact composition is not known, and therefore it is not possible to quantify the influence of

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unknown additives or crosslinker. Nevertheless also in this case it is possible to predict the order of the fluxes for different solvents, which demonstrates that solution-diffusion mechanism plays an important role, even if membranes have nanopores. It could be shown that the proposed approach brings advances in understanding of the transport mechanism in the membranes. These insights are important in future for both systematic membrane developments on the one hand, but also to dramatically reduce the experimental effort for membrane screening on the other.

The presented approach is compared to traditional state-of-the art semi-empirical equations. The approach of semi-empirical modelling is often essential for example in case when membrane material is unknown. The advantages and disadvantages of both modelling approaches in terms of experimental effort and suitability for different process development stages (membrane screening, process design) are discussed, as well as the possibility of their efficient combination.

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